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(71)Applicant : NISSAN MOTOR CO LTD

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(72)Inventor : IKEDA TAKUYA
KAMIKUBO MASANORI
KANESAKA HIROYUKI
MASUDA GOJI
TAKAGI HIROYUKI

(54) PRODUCTION OF ADSORPTIVE CATALYST FOR PURIFICATION OF EXHAUST GAS

(57)Abstract:

PURPOSE: To produce an adsorptive catalyst capable of efficiently adsorbing hydrocarbon in exhaust gas because hydrocarbon diffuse sufficiently even in the pores in zeolite.

CONSTITUTION: An inorg. binder, water and an org. emulsion are added to zeolite powder to prepare a slurry and this slurry is applied to a catalyst carrier, dried and fired.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the catalyst for emission gas purification characterized by adding an inorganic binder, water, and an organic emulsion to zeolite powder, forming a slurry, applying this slurry subsequently to catalyst support, and calcinating after drying.

[Claim 2] The manufacture approach of the adsorption catalyst for emission gas purification according to claim 1 characterized by using at least one sort chosen from the group which consists of mordenite, USY, a beta-zeolite, and ZSM-5 as a zeolite.

[Claim 3] Mordenite, beta-zeolite, and ZSM-5 are SiO₂ / aluminum 2O₃. It is the range of 50-2000 in a mole ratio, and USY is SiO₂ / aluminum 2O₃. The manufacture approach of the adsorption catalyst for emission gas purification according to claim 1 or 2 characterized by being the range of 50-300 in a mole ratio.

[Claim 4] The manufacture approach of the adsorption catalyst for emission gas purification according to claim 1 characterized by using the organic emulsion in the range of 10-1000nm particle size.

[Claim 5] The manufacture approach of the adsorption catalyst for emission gas purification by which it is making [support]-at least one sort of noble metals chosen from group which applies powder which used activity Seria and/or alumina as principal component on zeolite layer of catalyst acquired by approach according to claim 1, and consists of Pt, Pd, and Rh as catalyst component on this powder further characterized.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Since a hydrocarbon fully diffuses especially this invention in zeolite pore about the manufacture approach of the adsorption catalyst for emission gas purification, it relates to the manufacture approach of the adsorption catalyst for emission gas purification that the hydrocarbon in exhaust gas can be adsorbed efficiently.

[0002]

[Description of the Prior Art] Conventionally, as a catalyst for emission gas purification of internal combustion engines, such as an automobile, the catalyst which performs oxidation of a carbon monoxide (CO) and a hydrocarbon (HC) and reduction of nitrogen oxides (NOx) to coincidence is used widely. As such a catalyst, the thing which made the alumina coat layer on fireproof support support noble metals, such as Pd, Pt, and Rh, the thing which added base metal oxides, such as rare earth metals, such as Ce and La, and nickel, as a co-catalyst component if needed are proposed (JP,58-20307,B). The catalyst indicated by this official report is strongly influenced of exhaust gas temperature and an engine setting air-fuel ratio.

[0003] On the other hand, generally 300 degrees C or more of catalysts for automobiles are required for the exhaust gas temperature which demonstrates a purification function, and an air-fuel ratio is oxidization and NOX of HC and CO. A catalyst works most effectively near the theoretical air fuel ratio (A/F=14.6) which can balance reduction. Therefore, by automobile furnished with the exhaust gas purge using the conventional three way component catalyst, it is installed in a location which a three way component catalyst commits effectively, and the oxygen density of an exhaust air system is detected, and feedback control is performed so that gaseous mixture may be maintained near theoretical air fuel ratio.

[0004] However, even if it was the case where the conventional three way component catalyst was installed immediately after an exhaust manifold, immediately after engine starting with low (300 degrees C or less) exhaust gas temperature, catalytic activity was low and HC discharged in large quantities immediately after starting (at the time of a cold start) had the fault of being discharged as it is, without being purified. In order to solve this fault, the exhaust gas purge which has arranged the HC trapper which filled up the exhaust air upstream of a catalytic converter with the adsorption material for adsorbing cold HC is proposed (JP,2-211245,A, JP,2-135126,A). Moreover, combustible material is added in a catalyst slurry and the approach which improved gaseous diffusion nature is proposed (JP,61-245850,A).

[0005]

[Problem(s) to be Solved by the Invention] However, in the exhaust gas purge concerning above-mentioned JP,2-211245,A, since the foaming agent was used in order to form a stoma into a zeolite layer, there was a fault [loading] that a lifting and the coating nature to like were bad, at the time of a honeycomb coat. Moreover, in the exhaust gas purge concerning JP,2-135126,A, there was a fault that the particle diameter of the alumina sol currently used as a binder was fine, and could not form a stoma. Furthermore, although a stoma 10,000nm or more is formed and the gaseous diffusion nature to a catalytic activity point was raised by the approach concerning JP,61-245850,A, the fault that a hydrocarbon could not be diffused was in zeolite pore in the large stoma 10,000nm or more.

[0006] Therefore, since the purpose of this invention can form a stoma 10,000nm or less into a zeolite layer, and a hydrocarbon can fully diffuse it in ZEORATO pore and it can raise the adsorption capacity force, it is to offer the manufacture approach of the adsorption catalyst for emission gas purification that the hydrocarbon in exhaust gas can be adsorbed efficiently.

[0007]

[Means for Solving the Problem and its Function] In order to solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, this invention persons mixed the organic emulsion in the zeolite slurry, and the organic emulsion could decompose by calcinating behind a coat, they could form the stoma into the zeolite layer, and, as a result, the hydrocarbon diffused them in zeolite pore, and they reached [that the adsorption capacity force improves and] a header and this invention.

[0008] The above-mentioned purpose of this invention added an inorganic binder, water, and an organic emulsion to zeolite powder, formed the slurry, and was attained by the manufacture approach of the adsorption catalyst for emission gas purification characterized by applying this slurry subsequently to catalyst support, and calcinating after drying. Hereafter, this invention is further explained to a detail.

[0009] In the manufacture approach of this invention, an organic emulsion is mixed in the slurry which added and formed an inorganic binder, water, and an organic emulsion in zeolite powder, and it applies to catalyst support. Thereby, a stoma can be formed in 10-10,000nm into a zeolite layer. If a stoma is set to 10nm to the following, the poisoning matter sticks to a front face and a stoma blockades. Conversely, if it exceeds 10,000nm, a hydrocarbon cannot be diffused in zeolite pore.

[0010] It is desirable to use the mixing ratio (% of the weight) of a zeolite and an organic emulsion in 1:1-10:1. If a mixing ratio (% of the weight) becomes less than 1:1, the ratio of an organic emulsion increases, and since the total amount which can carry out a coat to a honeycomb is restricted, the amount of zeolite coats will decrease. Conversely, if 10:1 is exceeded, an emulsion ratio will become low too much and the gaseous diffusion nature effectiveness will not be acquired.

[0011] Although it can be used choosing suitably from well-known zeolites as a zeolite used in this invention, it is desirable especially to choose from ordinary temperature what has sufficient HC adsorption capacity and has high endurance even if it is comparatively high temperature and is moreover under a water existence ambient atmosphere. It is desirable to use at least one sort chosen from the group which consists of mordenite, USY, a beta-zeolite, and ZSM-5, for example as such a zeolite, the range of mordenite, beta-zeolite, and ZSM-5 is 50-2000 in SiO₂ / aluminum₂ O₃ mole ratio especially, and USY is SiO₂ / aluminum 2O₃. It is desirable that it is the range of 50-300 in a mole ratio. Mordenite, beta-zeolite, ZSM-5, and USY are SiO₂ / aluminum 2O₃. If it becomes less than 50 by the mole ratio, in order to adsorb alternatively the water molecule which lives together, hydrocarbon adsorption capacity falls. Conversely, if 2000 is exceeded by the mole ratio and USY exceeds [mordenite, beta-zeolite, and ZSM-5] 300 by the mole ratio, respectively, the amount of adsorption of a hydrocarbon will decrease. independent [, for example / in alumina sol, a silica sol, etc.] as an inorganic binder used in this invention -- or it can combine and use.

[0012] independent [, for example / in acrylic styrene copolymerization resin, vinyl acetate resin, acrylic copolymerization resin, styrene butadiene copolymerization resin, etc.] as an organic emulsion -- or it can combine and use. As for this organic emulsion, it is desirable that it is the range of 10-1000nm particle size, and it is especially desirable that it is the range which is 30-500nm. If an organic emulsion becomes the particle size of less than 10nm, the stoma which is in the range effective in an adsorption property of 10-10,000nm to a zeolite cannot be formed. on the contrary -- if particle size exceeds 1000nm -- a zeolite layer -- ** -- it becomes impossible to be able to become high, and for the coating nature to a honeycomb to fall, and to make the amount of purpose coats support

[0013] In this way, although only the adsorption catalyst obtained can fully adsorb a hydrocarbon, in order to equip an exhaust air system and to put in practical use, it is desirable to consider as the self-consecration type to which the engine performance which purifies the hydrocarbon from which it is desorbed with the rise of temperature was added and which coated the three way component catalyst layer on the adsorption layer (zeolite). That is, in this invention, the powder which used activity Seria and/or an alumina as the principal component can be applied on a zeolite layer, and it can have a catalyst bed containing at least one sort chosen from the group which consists of Pt, Pd,

and Rh as a catalyst component on the powder further.

[0014] It can be used in this invention, choosing suitably from well-known catalyst support as catalyst support, for example, monolith support, metal support, etc. are mentioned. Although not restricted, as for especially the configuration of this catalyst support, it is desirable to usually use it in a honeycomb configuration, and it applies catalyst powder to various honeycomb-like base materials, and is used for them. As this honeycomb material, although many things of the quality of cordierite are generally used, it is also possible to use the honeycomb which consists of a metallic material, and the catalyst powder itself may be further fabricated in a honeycomb configuration. By making the configuration of a catalyst into the shape of a honeycomb, since the touch area of a catalyst and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for automobiles, it is very advantageous.

[0015]

[Example] Hereafter, this invention is further explained in full detail according to an example. Unless it refuses especially in an example, the section shows the weight section.

[0016] the example 1 USY(SiO₂/aluminum₂ O₃ =50)100 section and an organic emulsion (acrylic ester copolymerization resin →) 45% per part, organic particle-size 34 sections of 100nm, and a silica sol (SiO₂ → 20%) pH2.7, particle-size the 150 sections of 7-9nm, the 10% nitric-acid 50 section, and the water 300 section were supplied to the magnetic pot, preferential grinding was carried out for 40 minutes or with universal ball mill equipment with vibration mill equipment for 6.5 hours, and the wash coat slurry was manufactured. After carrying out water absorption processing of the monolith support made from cordierite by the suction coat method, said manufactured slurry was supplied to homogeneity in the whole support cross section, and the excessive slurry was removed by the suction coat method. Subsequently, after drying the obtained slurry, temporary baking was carried out at 400 degrees C for 1 hour. Thereby, the coat of the USY was carried out to support in the amount of about 40 g/L coats. The above-mentioned wash coat, desiccation, and baking were repeated further 3 times, the coat of the zeolite of a total of 150 g/L was carried out, baking was performed at 650 degrees C in the air ambient atmosphere for 4 hours, and the adsorption catalyst -1 was acquired.

[0017] The example 2 organic emulsion 18 section was used, and also the adsorption catalyst -2 was acquired by the completely same approach as an example 1.

[0018] The example 3 USY(SiO₂/aluminum₂ O₃ =50)50 section and the ZSM-5 (SiO₂/aluminum₂ O₃ =700) 50 section were used, and also the adsorption catalyst -3 was acquired by the completely same approach as an example 1.

[0019] The example 4 beta zeolite (SiO₂/aluminum₂ O₃ =100) 50 section and the ZSM-5 (SiO₂/aluminum₂ O₃ =700) 50 section were used, and also the adsorption catalyst -4 was acquired by the completely same approach as an example 1.

[0020] The adsorption catalyst was acquired by the completely same approach as example 5 example 3. Subsequently, the activity Seria powder (henceforth Pt/CeO₂) 100 section which supported Pt, Supply the alumina 50 section and the 2% nitric-acid 150 section to a magnetic pot, and a WOSHU coat slurry is manufactured completely like an example 3. The coat of the Pt catalyst bed of 100 g/L was carried out on USY obtained above by the same approach as an example 3, and ZSM-5 mixolimnion, and baking of 4 hours was performed at 650 degrees C under the air ambient atmosphere after desiccation. Furthermore, the alumina powder (henceforth Rh/aluminum₂ O₃) 100 section which supported Rh, Supply the alumina 50 section and the 2% nitric-acid 150 section to a magnetic pot, and a WOSHU coat slurry is manufactured completely like the above. It is Pt/CeO₂ like the above. It is Rh/aluminum₂ O₃ of 50 g/L on a layer. The coat of the catalyst bed was carried out, after drying, baking of 4 hours was performed at 650 degrees C under the air ambient atmosphere, and the adsorption catalyst -5 was acquired.

[0021] Replaced with the activity Seria powder which supported example 6Pt, and alumina powder (henceforth Pd/aluminum₂ O₃) was used, and also the adsorption catalyst -6 was acquired by the completely same approach as an example 5.

[0022] An adsorption catalyst is acquired by the completely same approach as example 7 example 1, and it is Pt/CeO₂ on a USY layer by the approach completely same next as an example 5. The coat of the catalyst bed is carried out and it is Pt/CeO₂ by the completely still more nearly same

approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -7 was acquired.

[0023] An adsorption catalyst is acquired by the completely same approach as example 8 example 1, and it is Pd/aluminum 2O₃ on a USY layer by the approach completely same next as an example 6. The coat of the catalyst bed is carried out and it is Pd/aluminum 2O₃ by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -8 was acquired.

[0024] Replaced with example 9USY (SiO₂/aluminum 2 O₃ =50), and ZSM-5 (SiO₂/aluminum 2 O₃ =50) was used, and also the adsorption catalyst -9 was acquired by the completely same approach as an example 1.

[0025] Replaced with example 10USY (SiO₂/aluminum 2 O₃ =50), and used ZSM-5 (SiO₂/aluminum 2 O₃ =700), and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pt/CeO₂ on ZSM-five layers by the approach completely same next as an example 5. The coat of the catalyst bed is carried out. Furthermore, it is Pt/CeO₂ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -10 was acquired.

[0026] Replaced with example 11USY (SiO₂/aluminum 2 O₃ =50), and used ZSM-5 (SiO₂/aluminum 2 O₃ =700), and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O₃ on ZSM-five layers by the approach completely same next as an example 6. The coat of the catalyst bed is carried out. Furthermore, it is Pd/aluminum 2O₃ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -11 was acquired.

[0027] Replaced with example 12USY (SiO₂/aluminum 2 O₃ =50), and mordenite (SiO₂/aluminum 2 O₃ =200) was used, and also the adsorption catalyst -12 was acquired by the completely same approach as an example 1.

[0028] Replaced with example 13USY (SiO₂/aluminum 2 O₃ =50), and used mordenite (SiO₂/aluminum 2 O₃ =200), and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pt/CeO₂ on a mordenite layer by the approach completely same next as an example 5. The coat of the catalyst bed is carried out. Furthermore, it is Pt/CeO₂ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -13 was acquired.

[0029] Replaced with example 14USY (SiO₂/aluminum 2 O₃ =50), and used mordenite (SiO₂/aluminum 2 O₃ =200), and also Acquire an adsorption catalyst by the completely same approach as an example 1, and the coat of the 2OPd/aluminum 3 catalyst bed is carried out on a mordenite layer by the approach completely same next as an example 6. Furthermore, it is Pd/aluminum 2O₃ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -14 was acquired.

[0030] Replaced with example 15USY (SiO₂/aluminum 2 O₃ =50), and beta zeolite (SiO₂/aluminum 2 O₃ =100) was used, and also the adsorption catalyst -15 was acquired by the completely same approach as an example 1.

[0031] Replaced with example 16USY (SiO₂/aluminum 2 O₃ =50), and used beta zeolite (SiO₂/aluminum 2 O₃ =100), and also By the completely same approach as an example 1, acquire an adsorption catalyst, and the coat of the Pt/CeO₂ catalyst bed is carried out on beta zeolite layer by the approach completely same next as an example 5. Furthermore, it is Pt/CeO₂ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -16 was acquired.

[0032] Replaced with example 17USY (SiO₂/aluminum 2 O₃ =50), and used beta zeolite (SiO₂/aluminum 2 O₃ =100), and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O₃ on beta zeolite layer by the approach completely same next as an example 6. The coat of the catalyst bed is carried out. Furthermore, it is Pd/aluminum 2O₃ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -17 was acquired.

[0033] The example 18 mordenite (SiO₂/aluminum 2 O₃ =200) 50 section and the ZSM-5 (SiO₂/aluminum 2 O₃ =700) 50 section were used, and also the adsorption catalyst -18 was acquired

by the completely same approach as an example 1.

[0034] Used the example 19 mordenite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 200$) 50 section and the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 50 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pt/CeO₂ on mordenite, and ZSM-five layers by the approach completely same next as an example 5. The coat of the catalyst bed is carried out. Furthermore, it is Pt/CeO₂ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -19 was acquired.

[0035] Used the example 20 mordenite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 200$) 50 section and the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 50 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O₃ on mordenite, and ZSM-five layers by the approach completely same next as an example 6. The coat of the catalyst bed is carried out. Furthermore, it is Pd/aluminum 2O₃ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -20 was acquired.

[0036] Used the example 21 beta zeolite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 100$) 50 section and the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 50 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pt/CeO₂ on beta zeolite, and ZSM-five layers by the approach completely same next as an example 5. The coat of the catalyst bed is carried out. Furthermore, it is Pt/CeO₂ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -21 was acquired.

[0037] Used the example 22 beta zeolite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 100$) 50 section and the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 50 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O₃ on beta zeolite, and ZSM-five layers by the approach completely same next as an example 6. The coat of the catalyst bed is carried out. Furthermore, it is Pd/aluminum 2O₃ by the completely same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -22 was acquired.

[0038] The example 23 USY ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 50$) 33 section, the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 33 section, and the beta zeolite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 100$) 33 section were used, and also the adsorption catalyst -23 was acquired by the completely same approach as an example 1.

[0039] Used the example 24 USY ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 50$) 33 section, the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 33 section, and the beta zeolite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 100$) 33 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1. By the approach completely same next as an example 5 USY, It is Pt/CeO₂ on ZSM-5 and beta zeolite layer. The coat of the catalyst bed is carried out and it is Pt/CeO₂ by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -24 was acquired.

[0040] Used the example 25 USY ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 50$) 33 section, the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 33 section, and the beta zeolite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 100$) 33 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1. By the approach completely same next as an example 6 USY, It is Pd/aluminum 2O₃ on ZSM-5 and beta zeolite layer. The coat of the catalyst bed is carried out and it is Pd/aluminum 2O₃ by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O₃ on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -25 was acquired.

[0041] The example 26 USY ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 50$) 33 section, the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 33 section, and the mordenite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 200$) 33 section were used, and also the adsorption catalyst -26 was acquired by the completely same approach as an example 1.

[0042] Used the example 27 USY ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 50$) 33 section, the ZSM-5 ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 700$) 33 section, and the mordenite ($\text{SiO}_2/\text{aluminum}_2 \text{O}_3 = 200$) 33 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1. By the approach completely same next as an example 5 USY, It is Pt/CeO₂ on ZSM-5 and a mordenite layer. The coat of the catalyst bed is carried out and it is Pt/CeO₂ by the completely still more nearly same

approach as an example 5. It is Rh/aluminum 2O3 on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -27 was acquired.

[0043] Used the example 28USY(SiO2/aluminum2 O3 =50)33 section, the ZSM-5 (SiO2/aluminum2 O3 =700) 33 section, and the mordenite (SiO2/aluminum2 O3 =200) 33 section, and also An adsorption catalyst is acquired by the completely same approach as an example 1. By the approach completely same next as an example 6 USY, It is Pd/aluminum 2O3 on ZSM-5 and a mordenite layer. The coat of the catalyst bed is carried out and it is Pd/aluminum 2O3 by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O3 on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -28 was acquired.

[0044] The organic emulsion of 30nm of example 29 mean diameters was used, and also an adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O3 on a USY layer by the approach completely same next as an example 6. The coat of the catalyst bed is carried out and it is Pd/aluminum 2O3 by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O3 on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -29 was acquired.

[0045] The organic emulsion of 500nm of example 30 mean diameters was used, and also an adsorption catalyst is acquired by the completely same approach as an example 1, and it is Pd/aluminum 2O3 on a USY layer by the approach completely same next as an example 6. The coat of the catalyst bed is carried out and it is Pd/aluminum 2O3 by the completely still more nearly same approach as an example 5. It is Rh/aluminum 2O3 on a layer. The coat of the catalyst bed was carried out and the adsorption catalyst -30 was acquired.

[0046] Did not add an example of comparison 1 organic emulsion, the silica sol 215 same section as an example 1, the 10% nitric-acid water 100 section, and the water 15 section were used, and also the adsorption catalyst -31 was acquired by the completely same approach as an example.

[0047] Did not add an example of comparison 2 organic emulsion, USY (SiO2/aluminum2 O3 =7) was used, and also the adsorption catalyst -32 was acquired by the completely same approach as the example 1 of a comparison.

[0048] Did not add an example of comparison 3 organic emulsion, ZSM-5 (SiO2/aluminum2 O3 =22) was used, and also the adsorption catalyst -32 was acquired by the completely same approach as the example 1 of a comparison.

[0049] The organic emulsion of 1200nm of example of comparison 4 mean diameters was used, and also the adsorption catalyst -34 was acquired by the completely same approach as an example 1.

[0050] It equipped with the adsorption catalyst acquired in the above-mentioned examples 1-30 and the examples 1-5 of a comparison before the under floor catalyst, and HC adsorption / purification property was evaluated, comparing adsorption catalyst a non-equipped system with the engine performance. The evaluation result is shown in Tables 1 and 2.

[0051]

[Table 1]

| | 触媒番号 | H C 低減率 Abag 0~125 秒 | H C 低減率 Abag 0~505 秒 |
|--------|--------|-------------------------|-------------------------|
| 実施例 1 | 吸着触媒 1 | 45.6% | 0% |
| 実施例 2 | 同 2 | 41.4% | 0% |
| 実施例 3 | 同 3 | 47.0% | 0% |
| 実施例 4 | 同 4 | 50.2% | 0% |
| 実施例 5 | 同 5 | 50.1% | 15.3% |
| 実施例 6 | 同 6 | 51.7% | 17.4% |
| 実施例 7 | 同 7 | 41.4% | 13.0% |
| 実施例 8 | 同 8 | 41.4% | 13.5% |
| 実施例 9 | 同 9 | 38.8% | 0% |
| 実施例 10 | 同 10 | 38.8% | 6.1% |
| 実施例 11 | 同 11 | 38.8% | 6.4% |
| 実施例 12 | 同 12 | 39.8% | 0% |
| 実施例 13 | 同 13 | 39.8% | 9.0% |
| 実施例 14 | 同 14 | 39.8% | 9.0% |
| 実施例 15 | 同 15 | 44.9% | 0% |
| 実施例 16 | 同 16 | 44.8% | 15.3% |
| 実施例 17 | 同 17 | 44.8% | 15.5% |

[0052]

[Table 2]

| | 触媒番号 | H C 低減率 | H C 低減率 |
|--------|---------|---------|---------|
| 実施例 18 | 吸着触媒 18 | 41.7% | 0% |
| 実施例 19 | 同 19 | 41.7% | 13.1% |
| 実施例 20 | 同 20 | 41.7% | 13.2% |
| 実施例 21 | 同 21 | 51.1% | 17.7% |
| 実施例 22 | 同 22 | 51.2% | 17.7% |
| 実施例 23 | 同 23 | 51.7% | 0% |
| 実施例 24 | 同 24 | 51.7% | 18.1% |
| 実施例 25 | 同 25 | 51.7% | 18.2% |
| 実施例 26 | 同 26 | 50.0% | 0% |
| 実施例 27 | 同 27 | 49.9% | 15.1% |
| 実施例 28 | 同 28 | 50.0% | 15.2% |
| 実施例 29 | 同 29 | 41.3% | 13.5% |
| 実施例 30 | 同 30 | 41.8% | 13.6% |
| 比較例 1 | 同 31 | 39.4% | 0% |
| 比較例 2 | 同 32 | 2.0% | 0% |
| 比較例 3 | 同 33 | 36.9% | 0% |
| 比較例 4 | 同 35 | 39.5% | 0% |

[0053] In addition, in order to evaluate the adsorption capacity of HC discharged at the time of (1)

engine starting in evaluation, the emission decreasing rate for Abag0 - 125 seconds was measured.

(2) It ****s, before the three way component catalyst of an adsorption catalyst lower stream of a river also activates HC to which it stuck temporarily, and there is no emission fall effectiveness.

Then, in order to evaluate the desorption control ability and self-consecration ability by the adsorption catalyst, the emission decreasing rate for [Abag] 0 - 505 seconds was measured.

[0054] Evaluation condition adsorption catalyst capacity 1.3L evaluation car The Nissan Motor Co., Ltd. make, 3000 cc engine evaluation mode of V types LA4-CH (Abag)

[0055]

[Effect of the Invention] After coating a honeycomb with the mixed slurry of a zeolite and an organic emulsion, the manufacture approach of the catalyst for emission gas purification of this invention can form a stoma by calcinating because an organic emulsion decomposes. Therefore, according to the manufacture approach of the catalyst for emission gas purification of this invention, since gaseous diffusion nature improves to an adsorption site, the hydrocarbon in exhaust gas can be adsorbed efficiently.

[Translation done.]

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|-----------|----------------|----------|--|
| (21) 出願番号 | 特願平6-34658 | (71) 出願人 | 000003997 日産自動車株式会社 神奈川県横浜市神奈川区宝町2番地 |
| (22) 出願日 | 平成6年(1994)3月4日 | (72) 発明者 | 池田 卓弥 神奈川県横浜市神奈川区宝町2番地 日産 自動車株式会社内 |
| | | (72) 発明者 | 上久保 真紀 神奈川県横浜市神奈川区宝町2番地 日産 自動車株式会社内 |
| | | (72) 発明者 | 金坂 浩行 神奈川県横浜市神奈川区宝町2番地 日産 自動車株式会社内 |
| | | (74) 代理人 | 弁理士 杉村 暁秀 (外5名) 最終頁に続く |

(54) 【発明の名称】 排ガス浄化用吸着触媒の製造方法

(57) 【要約】

【目的】 炭化水素がゼオライト細孔中まで十分に拡散するので、排ガス中の炭化水素を効率良く吸着することのできる排ガス浄化用吸着触媒の製造方法を提供すること。

【構成】 ゼオライト粉末に無機バインダー、水及び有機エマルジョンを加えてスラリーを形成し、次いで該スラリーを触媒担体に塗布し、乾燥した後焼成することを特徴とする排ガス浄化用吸着触媒の製造方法。

【特許請求の範囲】

【請求項 1】ゼオライト粉末に無機バインダー、水及び有機エマルジョンを加えてスラリーを形成し、次いで該スラリーを触媒担体に塗布し、乾燥した後焼成することを特徴とする排ガス浄化用触媒の製造方法。

【請求項 2】ゼオライトとしてモルデナイト、USY、 β -ゼオライト及び ZSM-5 からなる群から選ばれた少なくとも 1 種を用いることを特徴とする請求項 1 記載の排ガス浄化用吸着触媒の製造方法。

【請求項 3】モルデナイト、 β -ゼオライト及び ZSM-5 が $\text{SiO}_2/\text{Al}_2\text{O}_3$ 、モル比で 50~2000 の範囲であり、USY が $\text{SiO}_2/\text{Al}_2\text{O}_3$ 、モル比で 50~300 の範囲であることを特徴とする請求項 1 又は 2 記載の排ガス浄化用吸着触媒の製造方法。

【請求項 4】粒径 10~1000 nm の範囲にある有機エマルジョンを用いることを特徴とする請求項 1 記載の排ガス浄化用吸着触媒の製造方法。

【請求項 5】請求項 1 記載の方法で得られた触媒のゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末を塗布し、更に該粉末上に触媒成分として Pt、Pd 及び Rh からなる群から選ばれた少なくとも 1 種の貴金属を担持させたことを特徴とする排ガス浄化用吸着触媒の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、排ガス浄化用吸着触媒の製造方法に関し、特に、炭化水素がゼオライト細孔中まで十分に拡散するので、排ガス中の炭化水素を効率良く吸着することのできる排ガス浄化用吸着触媒の製造方法に関する。

【0002】

【従来技術】従来、自動車等の内燃機関の排ガス浄化用触媒としては、一酸化炭素 (CO) 及び炭化水素 (HC) の酸化と、窒素酸化物 (NOx) の還元とを同時に行う触媒が汎用されている。このような触媒としては、耐火性担体上のアルミナコート層に、Pt、Pd、Rh 等の貴金属を担持させたもの、及び必要に応じて助触媒成分として Ce、La 等の希土類金属や Ni 等のベースメタル酸化物を添加したもの等が提案されている (特公昭 58-20307 号公報)。この公報に記載されている触媒は、排ガス温度及びエンジンの設定空燃比の影響を強く受ける。

【0003】一方、自動車用触媒が浄化機能を発揮する排ガス温度は、一般に 300℃ 以上必要であり、また空燃比は、HC 及び CO の酸化と NOx の還元とのバランスがとれる理論空燃比 ($A/F=14.6$) 付近で触媒が最も有効に働く。従って、従来の三元触媒を用いる排ガス浄化装置を取り付けた自動車では、三元触媒が有効に働くような位置に設置されており、また排気系の酸素濃度を検出して、混合気を理論空燃比付近に保つように

フィードバック制御が行われている。

【0004】しかしながら、従来の三元触媒をエキゾーストマニホールド直後に設置した場合であっても、排ガス温度が低い (300℃ 以下) エンジン始動直後には触媒活性が低く、始動直後 (コールドスタート時) に大量に排出される HC は浄化されずにそのまま排出されてしまうという欠点があった。この欠点を解決するため、触媒コンバータの排気上流側にコールド HC を吸着するための吸着材を充填した HC トラップを配置した排ガス浄化装置が提案されている (特開平 2-211245 号公報、特開平 2-135126 号公報)。また、触媒スラリー中に可燃性物質を添加し、ガス拡散性を改良した方法が提案されている (特開昭 61-245850 号公報)。

【0005】

【発明が解決しようとする課題】しかしながら、上記特開平 2-211245 号公報に係る排ガス浄化装置では、ゼオライト層中に小孔を形成するために発泡剤を用いているため、ハニカムコート時に目づまりを起こしやすく、コーティング性が悪いという欠点があった。また、特開平 2-135126 号公報に係る排ガス浄化装置では、バインダーとして使用しているアルミナゾルの粒子径が細かく、小孔を形成することができないという欠点があった。更に、特開昭 61-245850 号公報に係る方法では、10,000 nm 以上の小孔を形成して触媒活性点までのガス拡散性を向上させているが、10,000 nm 以上の大きい小孔ではゼオライト細孔内まで炭化水素を拡散することができないという欠点があった。

【0006】従って本発明の目的は、ゼオライト層中に 10,000 nm 以下の小孔を形成することができるため炭化水素がゼオライト細孔中まで十分に拡散し、その吸着能力を向上させることができるので、排ガス中の炭化水素を効率良く吸着することのできる排ガス浄化用吸着触媒の製造方法を提供することにある。

【0007】

【課題を解決するための手段及び作用】本発明者らは、上記課題を解決するために鋭意検討した結果、有機エマルジョンをゼオライトスラリー中に混合し、コート後に焼成することで有機エマルジョンが分解してゼオライト層中に小孔を形成することができ、その結果炭化水素がゼオライト細孔中まで拡散し、その吸着能力が向上することを見出し、本発明に到達した。

【0008】本発明の上記の目的は、ゼオライト粉末に無機バインダー、水及び有機エマルジョンを加えてスラリーを形成し、次いで該スラリーを触媒担体に塗布し、乾燥した後焼成することを特徴とする排ガス浄化用吸着触媒の製造方法により達成された。以下、本発明について更に詳細に説明する。

【0009】本発明の製造方法においては、ゼオライト

粉末に無機バインダー、水及び有機エマルジョンを加えて形成したスラリー中に有機エマルジョンを混合して、触媒担体に塗布する。これによりゼオライト層中に10～10,000nmの範囲で小孔を形成することができる。小孔が10nm未満になると、被毒物質が表面に吸着し、小孔が閉塞する。逆に10,000nmを超えると、ゼオライト細孔内まで炭化水素を拡散することができない。

【0010】ゼオライトと有機エマルジョンとの混合比(重量%)を1:1～10:1の範囲で用いることが好ましい。混合比(重量%)が1:1未満になると、有機エマルジョンの比率が高まり、ハニカムにコートすることができる総量が限られるため、ゼオライトコート量が減少する。逆に10:1を超えると、エマルジョン比率が低くなり過ぎガス拡散性効果が得られない。

【0011】本発明において使用するゼオライトとしては、公知のゼオライトの中から適宜選択して使用することができるが、特に常温から比較的高い温度で、しかも水存在雰囲気下であっても十分なHC吸着能を有し、且つ高い耐久性を有するものを選択することが好ましい。このようなゼオライトとしては、例えばモルデナイト、USY、β-ゼオライト及びZSM-5からなる群から選ばれた少なくとも1種を用いることが好ましく、特にモルデナイト、β-ゼオライト及びZSM-5がSiO₂/Al₂O₃モル比で50～2000の範囲であり、USYがSiO₂/Al₂O₃モル比で50～300の範囲であることが好ましい。モルデナイト、β-ゼオライト、ZSM-5及びUSYがSiO₂/Al₂O₃モル比で50未満になると、共存する水分子を選択的に吸着してしまうため、炭化水素吸着能が低下する。逆にモルデナイト、β-ゼオライト及びZSM-5がモル比で2000を、USYがモル比で300を、それぞれ超えると、炭化水素の吸着量が減少する。本発明において使用する無機バインダーとしては、例えば、アルミナゾルやシリカゾル等を、単独又は組み合わせて用いることができる。

【0012】有機エマルジョンとしては、例えばアクリル・スチレン共重合樹脂、酢酸ビニル樹脂、アクリル共重合樹脂、スチレン・ブタジエン共重合樹脂等を単独又は組み合わせて用いることができる。この有機エマルジョンは粒径10～1000nmの範囲であることが好ましく、特に30～500nmの範囲であることが好ましい。有機エマルジョンが粒径10nm未満になると、ゼオライトに対し吸着特性に有効な10～10,000nmの範囲にある小孔を形成することができない。逆に、粒径が1000nmを超えるとゼオライト層が高くなり、ハニカムへのコーティング性が低下し、目的コート量を担持させることができなくなる。

【0013】こうして得られる吸着触媒のみでも炭化水素を十分に吸着することができるが、排気系に装着して

実用化するためには温度の上昇と共に脱離する炭化水素を浄化する性能を追加した、吸着層(ゼオライト)上に三元触媒層をコーティングした自己浄化タイプとすることが好ましい。即ち、本発明においては、ゼオライト層上に活性セリア及び/又はアルミナを主成分とした粉末を塗布し、更にその粉末上に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を備えることができる。

【0014】本発明において触媒担体としては、公知の触媒担体の中から適宜選択して使用することができ、例えばモノリス担体やメタル担体などが挙げられる。この触媒担体の形状は、特に制限されないが、通常はハニカム形状で使用することが好ましく、ハニカム状の各種基材に触媒粉末を塗布して用いられる。このハニカム材料としては、一般にコージエライト質のものが多く用いられるが、金属材料からなるハニカムを用いることも可能であり、更には触媒粉末そのものをハニカム形状に成形しても良い。触媒の形状をハニカム状とすることにより、触媒と排気ガスの接触面積が大きくなり、圧力損失も抑えられるため自動車用として用いる場合に極めて有利である。

【0015】

【実施例】以下、本発明を実施例によって更に詳述する。実施例において特に断らない限り、部は重量部を示す。

【0016】実施例1

USY(SiO₂/Al₂O₃=50)100部、有機エマルジョン(アクリル酸エステル共重合樹脂、有機分45%、粒径100nm)34部、シリカゾル(SiO₂20%、pH2.7、粒径7～9nm)150部、10%硝酸50部及び水300部を磁性ポットに投入し、振動ミル装置で40分間又はユニバーサルボールミル装置で6.5時間混合粉碎して、ウォッシュコートスラリーを製造した。コーディエライト製モノリス担体を吸引コート法で吸水処理した後、前記製造したスラリーを担体断面全体に均一に投入し、吸引コート法で余分なスラリーを除去した。次いで、得られたスラリーを乾燥した後、400℃で1時間仮焼成した。これによりUSYが約40g/Lコート量で担体にコートされた。上記ウォッシュコート、乾燥、焼成をさらに3回繰り返して合計150g/Lのゼオライトをコートし、空気雰囲気中で650℃で4時間焼成を行い、吸着触媒-1を得た。

【0017】実施例2

有機エマルジョン18部を用いた他は、実施例1と全く同様な方法により、吸着触媒-2を得た。

【0018】実施例3

USY(SiO₂/Al₂O₃=50)50部及びZSM-5(SiO₂/Al₂O₃=700)50部を用いた他は、実施例1と全く同様な方法により、吸着触媒-3を得た。

【0019】実施例4

β ゼオライト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) 50部及びZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒-4を得た。

【0020】実施例5

実施例3と全く同様な方法で吸着触媒を得た。次いでPtを担持した活性セリア粉末（以下、Pt/CeO₂、という）100部、アルミナ50部及び2%硝酸150部を磁性ポットに投入し、実施例3と全く同様にしてウォッシュコートスラリーを製造し、実施例3と同一の方法で上記で得られたUSY及びZSM-5混合層上に100g/LのPt触媒層をコートし、乾燥後、空気雰囲気下で650℃にて4時間の焼成を行った。更に、Rhを担持したアルミナ粉末（以下、Rh/Al₂O₃、という）100部、アルミナ50部及び2%硝酸150部を磁性ポットに投入し、前記と全く同様にしてウォッシュコートスラリーを製造し、前記と同様にしてPt/CeO₂層上に50g/LのRh/Al₂O₃触媒層をコートし、乾燥した後に、空気雰囲気下で650℃にて4時間の焼成を行い、吸着触媒-5を得た。

【0021】実施例6

Ptを担持した活性セリア粉末に代えてアルミナ粉末（以下、Pd/Al₂O₃、という）を用いた他は、実施例5と全く同様な方法で吸着触媒-6を得た。

【0022】実施例7

実施例1と全く同様な方法により吸着触媒を得、次に実施例5と全く同様な方法によりUSY層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-7を得た。

【0023】実施例8

実施例1と全く同様な方法により吸着触媒を得、次に実施例6と全く同様な方法によりUSY層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-8を得た。

【0024】実施例9

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) を用いた他は、実施例1と全く同様な方法により吸着触媒-9を得た。

【0025】実施例10

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$) を用いた他は、実施例1と全く同様な方法により吸着触媒を得、次に実施例5と全く同様な方法によりZSM-5層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-10を得た。

【0026】実施例11

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$) を用いた他は、実施例1と全く同様な方法により吸着触媒を得、次に実施例6と全く同様な方法によりZSM-5層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-11を得た。

【0027】実施例12

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてモルデナイト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$) を用いた他は、実施例1と全く同様な方法により吸着触媒-12を得た。

【0028】実施例13

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてモルデナイト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$) を用いた他は、実施例1と全く同様な方法により吸着触媒を得、次に実施例5と全く同様な方法によりモルデナイト層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-13を得た。

【0029】実施例14

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えてモルデナイト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$) を用いた他は、実施例1と全く同様な方法により吸着触媒を得、次に実施例6と全く同様な方法によりモルデナイト層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-14を得た。

【0030】実施例15

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えて β ゼオライト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) を用いた他は、実施例1と全く同様な方法により、吸着触媒-15を得た。

【0031】実施例16

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えて β ゼオライト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例5と全く同様な方法により β ゼオライト層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-16を得た。

【0032】実施例17

USY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) に代えて β ゼオライト ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法により β ゼオライト層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-17を得た。

【0033】実施例18モルデナイト ($\text{SiO}_2/\text{Al}_2\text{O}_3$)

、 $O_2 = 200$) 50部及びZSM-5 ($SiO_2 / Al_2O_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒-18を得た。

【0034】実施例19

モルデナイト ($SiO_2 / Al_2O_3 = 200$) 50部及びZSM-5 ($SiO_2 / Al_2O_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例5と全く同様な方法によりモルデナイト及びZSM-5層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-19を得た。

【0035】実施例20

モルデナイト ($SiO_2 / Al_2O_3 = 200$) 50部及びZSM-5 ($SiO_2 / Al_2O_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりモルデナイト及びZSM-5層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-20を得た。

【0036】実施例21

βゼオライト ($SiO_2 / Al_2O_3 = 100$) 50部及びZSM-5 ($SiO_2 / Al_2O_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例5と全く同様な方法によりβゼオライト及びZSM-5層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-21を得た。

【0037】実施例22

βゼオライト ($SiO_2 / Al_2O_3 = 100$) 50部及びZSM-5 ($SiO_2 / Al_2O_3 = 700$) 50部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりβゼオライト及びZSM-5層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-22を得た。

【0038】実施例23

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びβゼオライト ($SiO_2 / Al_2O_3 = 100$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒-23を得た。

【0039】実施例24

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びβゼオライト ($SiO_2 / Al_2O_3 = 100$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒

を得、次に実施例5と全く同様な方法によりUSY、ZSM-5及びβゼオライト層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-24を得た。

【0040】実施例25

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びβゼオライト ($SiO_2 / Al_2O_3 = 100$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりUSY、ZSM-5及びβゼオライト層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-25を得た。

【0041】実施例26

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びモルデナイト ($SiO_2 / Al_2O_3 = 200$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒-26を得た。

【0042】実施例27

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びモルデナイト ($SiO_2 / Al_2O_3 = 200$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例5と全く同様な方法によりUSY、ZSM-5及びモルデナイト層上にPt/CeO₂触媒層をコートし、更に実施例5と全く同様な方法によりPt/CeO₂層上にRh/Al₂O₃触媒層をコートし、吸着触媒-27を得た。

【0043】実施例28

USY ($SiO_2 / Al_2O_3 = 50$) 33部、ZSM-5 ($SiO_2 / Al_2O_3 = 700$) 33部及びモルデナイト ($SiO_2 / Al_2O_3 = 200$) 33部を用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりUSY、ZSM-5及びモルデナイト層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-28を得た。

【0044】実施例29

平均粒径30nmの有機エマルジョンを用いた他は、実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりUSY層上にPd/Al₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/Al₂O₃層上にRh/Al₂O₃触媒層をコートし、吸着触媒-29を得た。

【0045】実施例30

平均粒径500nmの有機エマルジョンを用いた他は、

実施例1と全く同様な方法により、吸着触媒を得、次に実施例6と全く同様な方法によりUSY層上にPd/A1₂O₃触媒層をコートし、更に実施例5と全く同様な方法によりPd/A1₂O₃層上にRh/A1₂O₃触媒層をコートし、吸着触媒-30を得た。

【0046】比較例1

有機エマルジョンを添加せず、実施例1と同様のシリカゾル215部、10%硝酸水100部及び水15部を用いた他は、実施例と全く同様な方法により、吸着触媒-31を得た。

【0047】比較例2

有機エマルジョンを添加せず、USY(SiO₂/Al₂O₃=7)を用いた他は、比較例1と全く同様な方法により、吸着触媒-32を得た。

*【0048】比較例3

有機エマルジョンを添加せず、ZSM-5(SiO₂/Al₂O₃=22)を用いた他は、比較例1と全く同様な方法により、吸着触媒-32を得た。

【0049】比較例4

平均粒径1200nmの有機エマルジョンを用いた他は、実施例1と全く同様な方法により、吸着触媒-34を得た。

【0050】上記実施例1~30及び比較例1~5で得られた吸着触媒を、床下触媒の前に装着し、HC吸着・浄化特性を吸着触媒未装着システムと性能を比較しつつ評価した。その評価結果を表1及び2に示す。

【0051】

*【表1】

| | 触媒番号 | HC低減率 Abag 0~125 秒 | HC低減率 Abag 0~505 秒 |
|--------|--------|-----------------------|-----------------------|
| 実施例 1 | 吸着触媒 1 | 45.6% | 0% |
| 実施例 2 | 同 2 | 41.4% | 0% |
| 実施例 3 | 同 3 | 47.0% | 0% |
| 実施例 4 | 同 4 | 50.2% | 0% |
| 実施例 5 | 同 5 | 50.1% | 15.3% |
| 実施例 6 | 同 6 | 51.7% | 17.4% |
| 実施例 7 | 同 7 | 41.4% | 13.0% |
| 実施例 8 | 同 8 | 41.4% | 13.5% |
| 実施例 9 | 同 9 | 38.8% | 0% |
| 実施例 10 | 同 10 | 38.8% | 6.1% |
| 実施例 11 | 同 11 | 38.8% | 6.4% |
| 実施例 12 | 同 12 | 39.8% | 0% |
| 実施例 13 | 同 13 | 39.8% | 9.0% |
| 実施例 14 | 同 14 | 39.8% | 9.0% |
| 実施例 15 | 同 15 | 44.9% | 0% |
| 実施例 16 | 同 16 | 44.8% | 15.3% |
| 実施例 17 | 同 17 | 44.8% | 15.5% |

【0052】

【表2】

| | 触媒番号 | H C低減率 | H C低減率 |
|--------|---------|--------|--------|
| 実施例 18 | 吸着触媒 18 | 41.7% | 0% |
| 実施例 19 | 同 19 | 41.7% | 13.1% |
| 実施例 20 | 同 20 | 41.7% | 13.2% |
| 実施例 21 | 同 21 | 51.1% | 17.7% |
| 実施例 22 | 同 22 | 51.2% | 17.7% |
| 実施例 23 | 同 23 | 51.7% | 0% |
| 実施例 24 | 同 24 | 51.7% | 18.1% |
| 実施例 25 | 同 25 | 51.7% | 18.2% |
| 実施例 26 | 同 26 | 50.0% | 0% |
| 実施例 27 | 同 27 | 49.9% | 15.1% |
| 実施例 28 | 同 28 | 50.0% | 15.2% |
| 実施例 29 | 同 29 | 41.3% | 13.5% |
| 実施例 30 | 同 30 | 41.8% | 13.6% |
| 比較例 1 | 同 31 | 39.4% | 0% |
| 比較例 2 | 同 32 | 2.0% | 0% |
| 比較例 3 | 同 33 | 36.9% | 0% |
| 比較例 4 | 同 35 | 39.5% | 0% |

【0053】尚、評価に当たっては、(1)エンジン始動時に排出されるH Cの吸着能を評価するためA b a g 0～125秒間のエミッション低下率を測定した。

(2)一時的に吸着したH Cも吸着触媒下流の三元触媒が活性化する前に脱離してエミッション低下効果が無い。そこで吸着触媒による脱離抑制能及び自己浄化能を評価するため、A b a g 0～505秒間のエミッション 30 低下率を測定した。

【0054】評価条件

吸着触媒容量

1.3 L

評価車両

日産自動車株式会社製、V型3*

*000ccエンジン

評価モード

LA4-CH (A b a g)

【0055】

【発明の効果】本発明の排ガス浄化用触媒の製造方法は、ゼオライトと有機エマルジョンとの混合スラリーをハニカムにコーティングした後、焼成することにより有機エマルジョンが分解することで小孔を形成することができる。従って本発明の排ガス浄化用触媒の製造方法によれば、吸着サイトまでガス拡散性が向上するので、排ガス中の炭化水素を効率良く吸着することができる。

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(72)発明者 増田 剛司

神奈川県横浜市神奈川区宝町2番地 日産自動車株式会社内

(72)発明者 高木 宏行

千葉県習志野市谷津5-32-9